UCRL-JC-135086
PREPRINT

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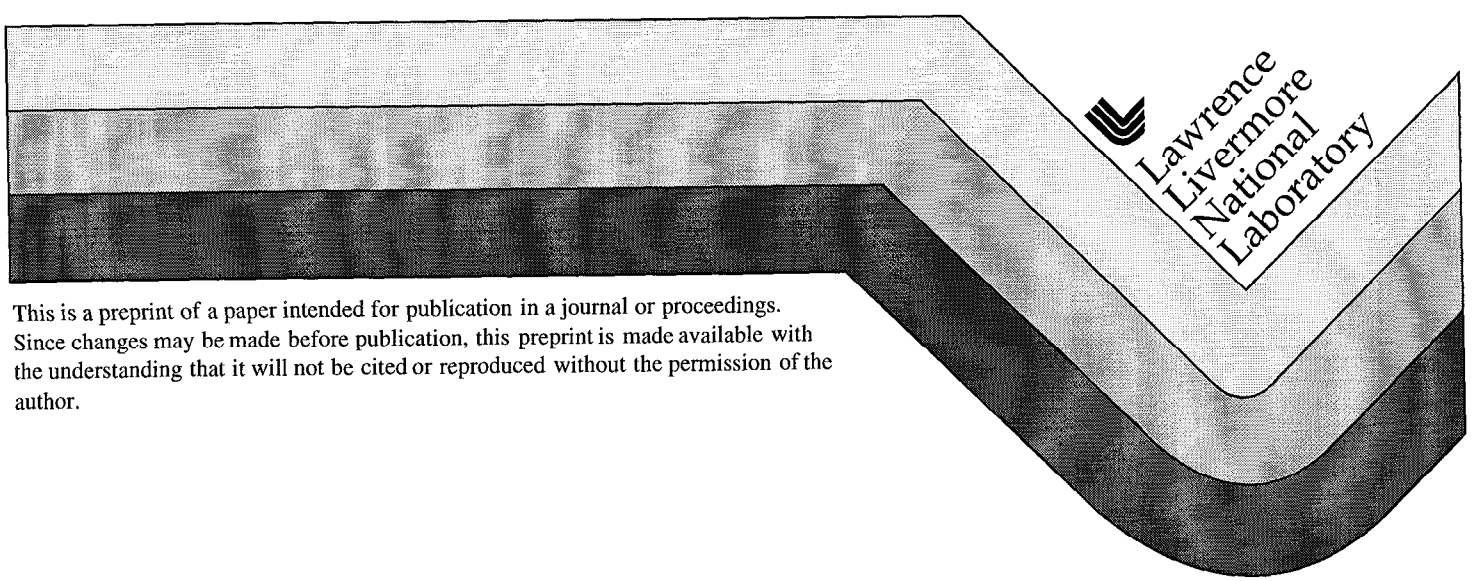
This paper was prepared for submittal to the
Fifth International Conference on the
Science and Technology of Display Phosphors
San Diego, California
November 8-10, 1999

June 1999



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Investigation of Long-Term Time Dependencies of Cathodoluminescence in Thin Film Oxide Phosphors for Field Emission Displays

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Introduction

Thin film oxide phosphors are prospective for low-voltage field-emission display applications due to their appropriate color coordinates, high efficiency[1,2], and possibility of creation of increased conductivity[3] in them. Long-term stability of phosphors is also very important for practical application. Therefore, long-term stability of the most efficient thin film oxide phosphors Y_2O_3:Eu, Zn_2SiO_4:Mn, Zn_2SiO_4:Ti, and Y_2SiO_5:Ce was investigated in present work.

Experimental techniques

Thin films were deposited with standard rf-magnetron sputtering and rf-diode deposition. Modified rf-magnetron method [4] also was used. Parameters of thin film phosphors were modified using high-temperature recrystallization at 900 – 1100 °C. Film structure was investigated with X-ray diffractometer HZG-4A with CuK_α radiation; crystal structure parameters were determined using software package "CSD". Cathodoluminescence (CL) was studied under electron excitation with energy of 0.5 – 3 keV.

Results and Discussion

The processes of long time behavior and degradation of phosphors under e-beam exposure are complex enough and depend on large number of factors. Usually to a first approximation the process of phosphors degradation can be described [5] as:

$$I = I_0/(1 + cN), \qquad (1)$$

where I_0 – primary intensity of luminescence,

I – intensity of irradiated phosphor,

c – "burning" parameter, cm^2,

N – total number of electrons hit 1 cm^2 exposed area.

In order to evaluate degradation parameters of thin film phosphors under electron excitation the method of accelerated testing of degradation processes was developed. The samples were measured (Fig 1) in laboratory-made CRT-prototype. Measured phosphor sample was permanently irradiated by electrons in a spot of small diameter with relatively large current densities at which total irradiation doze will be the same as at "normal" current densities, but for much longer period of time. As a reference intensity I_0 the intensity of spot periodically deflected to a non-irradiated region near the permanent position of spot was used in order to avoid nonstabilities. The spot size in our measurements was near 2 mm diameter; the excitation parameters were: V = 2 keV and e-beam current – 50 mkA. This mode of measurements during 8 hours corresponds to approximately 1500 hours of excitation of conventional 21-inch kinescope at 25 kV and 1 mA (assuming equal deposited charges per square cm during irradiation).

From these measurements the obtained value of burning parameter c for Y_2O_3:Eu thin film phosphor was 0.061·10–19 cm^2, for Zn_2SiO_4:Mn c = 0.057·10-19 cm^2, for Y_2SiO_5:Ce c = 0.184·10–19 cm^2, and for Zn_2SiO_4:Ti c = 0.370·10–19 cm^2 (Table.1). Measurements of CL spectra during e-beam irradiation have not shown any essential changes in spectra for all phosphors investigated. So the degradation might be caused by transformation in the lattice of phosphor itself.

From the results of our investigations it was found that degradation processes in a number of oxide thin films behave in a manner which differs from stated above [5] (formula 1). Analysis of long-term time dependencies of CL showed that in the case of thin films Y_2O_3:Eu, Y_2SiO_5:Ce, and Zn_2SiO_4:Ti they can be described as

$$I = I_0 / (K \cdot t^{1/2} + 1), \qquad (2)$$

where K – coefficient, which is proportional to tangent of slope angle and degradation rate,

t – time of irradiation of phosphor.

According to this law the experimental data in coordinates $(I_0/I - 1) = K \cdot t^{1/2}$ represent straight lines with different slope for different phosphors (Fig. 2). The values of coefficient K which is

proportional to tangent of slope angle and degradation rate were $1.26 \cdot 10^{-2}$, $3.62 \cdot 10^{-2}$, and $11.53 \cdot 10^{-2}$ for Y_2O_3:Eu, Y_2SiO_5:Ce and Zn_2SiO_4:Ti, respectively (Table.1). Such proportional to $t^{1/2}$ dependence is most likely to be caused by diffusion processes[6] during e-beam irradiation. The behavior of Zn_2SiO_4:Mn phosphor does not fit this dependency which indicates on different mechanism of degradation. During the initial part of exposure time the intensity of CL slightly decreases, and later on it increases to initial level. The results obtained has shown that blue thin film phosphor Zn_2SiO_4:Ti is less stable under long-term e-beam irradiation in the field-emission devices. The reason could be that Ti can create several types of luminescent centers in Zn_2SiO_4 and Ti^{4+} blue luminescence centers may transform in other less efficient centers of luminescence. The Y_2SiO_5:Ce thin film phosphor is more stable. The best long-term stability under low-energy e-beam excitation showed Y_2O_3:Eu and Zn_2SiO_4:Mn thin film phosphors which is the same as in the best industrial kinescope phosphors [7] at high-energy (25-30 keV) e-beam excitation.

Conclusions

Dependencies of luminescence intensities of thin film oxide phosphors on electron beam energy and current density were investigated. Long-term stability, as well as the degradation parameters of Y_2O_3:Eu, Zn_2SiO_4:Mn, Zn_2SiO_4:Ti, and Y_2SiO_5:Ce thin film phosphors were investigated. The best long-term stability under low-energy e-beam excitation showed Y_2O_3:Eu and Zn_2SiO_4:Mn thin film phosphors. The novel time behavior characteristic for degradation processes in thin films was found.

Acknowledgements

This work is supported by the USA through the Science and Technological Center in Ukraine (Project No.613), and Sandia National Laboratory, Livermore, CA, (Contract AO-5706). The work of TEF was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48

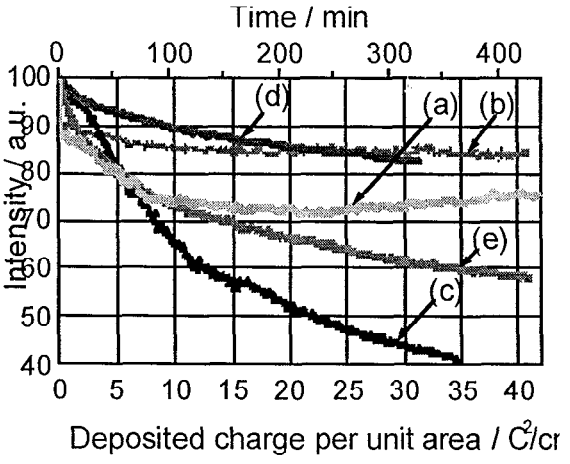

Fig.1. Degradation curves of thin film phosphor samples at 2 keV excitation: Zn_2SiO_4:Mn (a, b), Zn_2SiO_4:Ti (c), Y_2O_3:Eu (d).

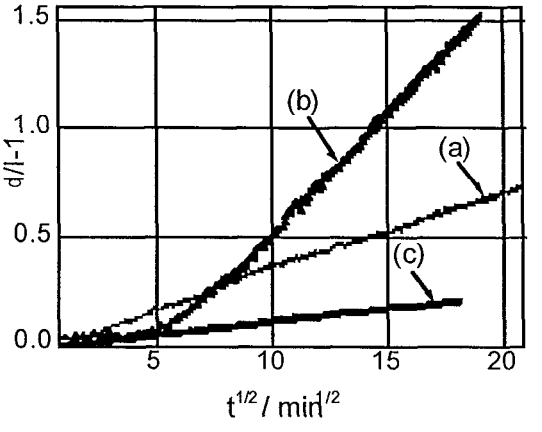

Fig.2. $(I_0/I - 1)$ vs. $t^{1/2}$ plot of degradation curves of thin-film phosphors Y_2SiO_5:Ce(a), Zn_2SiO_4:Ti (b), Y_2O_3:Eu (c).

Table 1. Electrical parameters of oxide conductive thin films phosphors.

Phosphor	Powder Phosphors [1] 25 keV		Thin films (this work) 2 keV	
	Electrical charge, decreasing intensity for 2 times, Coulombs	Burning parameter $c \cdot 10^{19}$, cm^2; Formula – (1)		Coefficient of degradation K; Formula – (2)
ZnS-CdS-Cu	11.9	0.140		
ZnS-CdS-Ag	4.5	0.370		
ZnS-Ag	9.9	0.170		
Zn_2SiO_4-Mn	104.0	0.016	0.057	no degradation
CaO-MgO-SiO_2-Ti	55.5	0.030		
ZnO-BeO-SiO_2-Mn	83.3	0.020		
ZnO-Zn	33.5	0.050		
$CaWO_4$	16.6	0.100		
Y_2O_3:Eu			0.061	0.013
Y_2SiO_5:Ce			0.184	0.036
Zn_2SiO_4:Ti			0.370	0.115

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